STANFORD UNIVERSITY LIBRARY
4
1920

A Study of the System Lithium Perchlorate and Water

A THESIS

THIS THESIS HAS BEEN ACCEPTED BY THE GRADUATE SCHOOL OF NEW YORK UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

By

CLARENCE D. L. ROPP

A. B.- West Virginia University 1921
M. A.- West Virginia University 1923

STANFORD UNIVERSITY LIBRARIES
WITHDRAWN

3781
153R
UNCLASSED

Graduate School
New York University
1925

[Reprint from the Journal of the American Chemical Society, 50, 1650 (1928).]

[Contribution from the Chemical Department of New York University]

THE SYSTEM LITHIUM PERCHLORATE–WATER

By John P. Simmons and Clarence D. L. Ropp[1]

Received March 27, 1928 Published June 5, 1928

According to A. Potilitzin,[2] aqueous solutions of lithium perchlorate give the trihydrate, $LiClO_4 \cdot 3H_2O$, which loses approximately two-thirds of its combined water when heated between 98 and 100°, changing to monohydrate, and all of its water between 130 and 150°. The approximate nature of these data makes apparent the need of a more careful study of this system.

Preparation of Lithium Perchlorate

Anhydrous lithium perchlorate was made by the method of Richards and Willard.[3] The purity of the salt was proved by a modification of a

[1] The results of this investigation were submitted by Clarence D. L. Ropp as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Potilitzin, *J. Russ. Phys.-Chem. Soc.*, **19**, 339 (1887); **20**, 541 (1888).

[3] Richards and Willard, This Journal, **32**, 4 (1910).

method by Lamb[4] for the analysis of perchlorates. This consists in heating a weighed amount of lithium perchlorate in a Pyrex test-tube loosely plugged with asbestos. The loss in weight is assumed to be due to the oxygen driven off. As an illustration, two such determinations gave 100.10 and 100.15% of lithium perchlorate.

Procedure

In order to establish accurately the number and composition of the hydrates of lithium perchlorate capable of existing between 0° and the temperature where the anhydrous salt is stable, the following experiments were made.

(1) Saturated solutions of lithium perchlorate were cooled from temperatures between 0 and 90°, approximately. As a result, long, needle shaped crystals formed which, after careful drying between filter paper, showed upon analysis a water content of 33.90%, which agrees well with the corresponding theoretical value for the trihydrate, 33.68%.

(2) A quantity of this trihydrate was powdered and placed in a desiccator over anhydrous lithium perchlorate and kept thus for a period of six weeks. This experimental arrangement causes the trihydrate to change to the next lower hydrate. Determinations of the water content of the specimen were made at frequent intervals and the percentage of water finally became constant at 14.52%. The theoretical value for $LiClO_4 \cdot H_2O$ is 14.48%.

(3) A synthetic lithium perchlorate monohydrate was made and this was used as a desiccating agent for crystals obtained by cooling solutions saturated between 0 and 90° and which by experiment[2] were proved to be $LiClO_4 \cdot 3H_2O$. The latter showed constancy in water content at 33.66%, which agrees with the corresponding value for $LiClO_4 \cdot 3H_2O$, 33.68%.

The results of these three sets of experiments indicate that lithium perchlorate forms two hydrates, $LiClO_4 \cdot 3H_2O$ and $LiClO_4 \cdot H_2O$ and that evidence of the existence of a dihydrate does not exist. The system was not investigated below 0°.

To obtain more precise information regarding the transition points involved in this system, solubility measurements were made over a temperature range from 0 to 170°. These measurements were made at the lower temperatures by agitating an excess of anhydrous salt with water in a solubility tube kept at constant temperature in a thermostat until constancy in concentration was reached. These determinations were supplemented by results obtained by sealing in a tube known quantities of anhydrous lithium perchlorate and water, immersing the tube in water and gradually heating until the solid phase disappeared. The tube was

[4] Lamb and Marden, THIS JOURNAL, 34, 812 (1912).

then cooled until the hydrate, stable at the temperature being used, crystallized out. The tube was then heated carefully one-tenth of a degree at a time with constant agitation and the temperature noted at which the last trace of solid phase disappeared. The solubility measurements at the higher temperatures were all made by the second method. Solubility data for the temperatures indicated are given in Table I.

TABLE I

SOLUBILITY OF $LiClO_4$ IN GRAMS PER 100 OF SOLUTION

Temp., °C.	Concn.	Temp., °C.	Concn.	Temp., °C.	Concn.
0[a]	29.90	92.3	62.5	108.9	72.8
10	32.88	94.3	65.0	120.7	75.0
20	35.95	95.1	66.32	136.9	80.0
25	37.48	94.8	66.67	144.0	82.5
30	38.87	93.2	70.0	148.5	85.0
40	41.97	92.7	70.3	149.3	87.5
64.6	50.0	92.53	70.33	144.2	90.0
77.9	55.0	93.2[b]	70.5	167.5[c]	91.04
89.2	60.0	97.3	71.0	172	91.11

[a] Trihydrate is solid phase.
[b] Monohydrate is solid phase.
[c] Anhydrous salt is solid phase.

Density values of the saturated solutions at the lower temperatures were made by weighing a known volume and are given in Table II.

TABLE II

DENSITIES OF SATURATED SOLUTIONS OF $LiClO_4$

0°	10°	20°	25°	30°	40°
1.215	1.236	1.258	1.269	1.277	1.300

H. H. Willard and G. F. Smith[5] determined the solubility of lithium perchlorate in water at 25°, obtaining a value of 37.385% and a density of 1.268, which agree very well with our values of 37.48% and a density of 1.269.

The melting point of anhydrous lithium perchlorate was determined by Potilitzin[2] and by Richards and Willard[3] as 236°, and this value was used in the construction of the solubility curve in Fig. 1. An inspection of the solubility curve of lithium perchlorate, Fig. 1, indicates clearly two transition temperatures and two congruent melting points. The melting point of $LiClO_4 \cdot 3H_2O$ from the curve is 95.1°, which agrees well with Potilitzin's[2] value of 95°. The melting point of $LiClO_4 \cdot H_2O$ from the curve is 149° for a content of 86.5% of $LiClO_4$. The theoretical value is 85.52%.

In order to determine the transition points with greater accuracy than could be attained by use of the solubility data, cooling experiments were

[5] Willard and Smith, THIS JOURNAL, 45, 286 (1923).

performed. Marked halts in temperature drop were observed at 92.53 and 145.75°. These temperature points indicate the transition points for $LiClO_4 \cdot 3H_2O \rightleftarrows LiClO_4 \cdot H_2O$ and $LiClO_4 \cdot H_2O \rightleftarrows LiClO_4$, respectively.

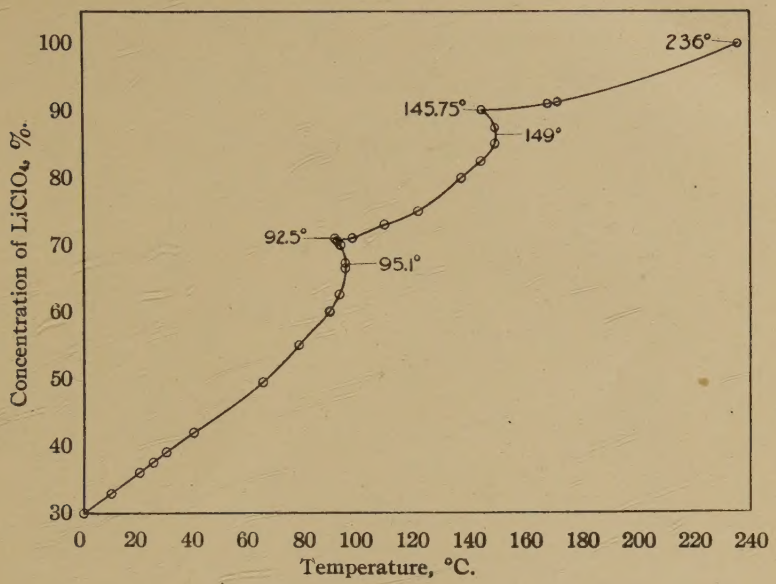


Fig. 1.

Summary

1. Solubility measurements of $LiClO_4$ in water over a temperature range from 0 to 170° have been made.

2. Density values of the saturated solutions over a temperature range from 0 to 40° have been made.

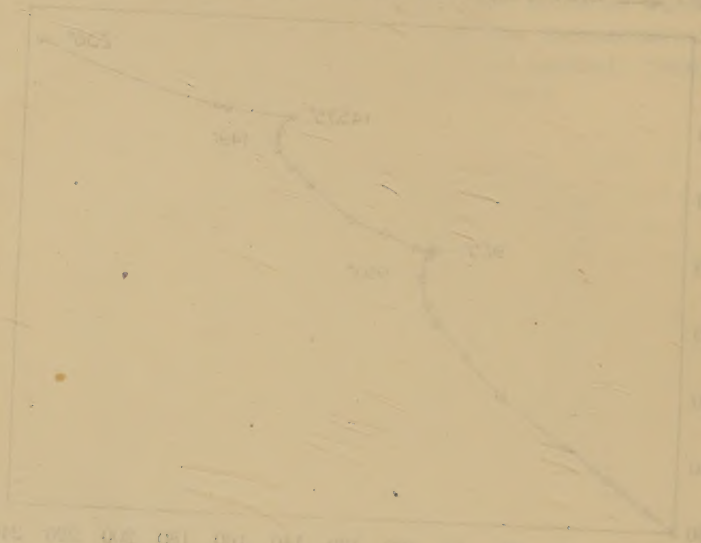
3. The existence of $LiClO_4 \cdot 3H_2O$ and $LiClO_4 \cdot H_2O$ is definitely established.

4. No evidence of the existence of a dihydrate was observed.

5. The transition point $LiClO_4 \cdot 3H_2O \rightleftarrows LiClO_4 \cdot H_2O$ is 92.53°.

6. The transition point $LiClO_4 \cdot H_2O \rightleftarrows LiClO_4$ is 145.75°.

7. The melting point of $LiClO_4 \cdot 3H_2O$ is confirmed at 95.1°.

8. The melting point of $LiClO_4 \cdot H_2O$ is 149°.

NEW YORK CITY